(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 September 2002 (19.09.2002)

PCT

(10) International Publication Number
WO 02/072701 A1

(51) International Patent Classification[7]: C08L 75/04, C08K 7/28

(21) International Application Number: PCT/GB02/00946

(22) International Filing Date: 8 March 2002 (08.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0105667.0 8 March 2001 (08.03.2001) GB

(71) Applicant *(for all designated States except US)*: **HYPER-LAST LIMITED** [GB/GB]; Station Road, Birch Vale, High Peak, Derbyshire SK22 1BR (GB).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **HARGREAVES, John** [GB/GB]; 69 Stitch Lane, Birch Vale, High Peak, Derbyshire SK22 1AW (GB). **MILLER, Matthew** [GB/GB]; 106 Hollins Lane, Marple Bridge, Cheshire SK6 5DA (GB).

(74) Agents: **MIDDLEMIST, I., A.** et al.; Wilson Gunn M'Caw, 41-51 Royal Exchange, Cross Street, Manchester M2 7BD (GB).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/072701 A1

(54) Title: IMPROVEMENTS IN INSULATING MATERIALS

(57) Abstract: Polyurethane precursor components are mixed on site immediately prior to or concurrently with application of the mixed and reacting polyurethane to a site of use, in separate mixing stages wherein in one stage at least one precursor component is mixed with glass or other microspheres, and in a second concurrent or immediately prior or subsequent mixing stage wherein the precursor components are mixed to form a polyurethane reaction mixture which is applied to the site of use. One or both of the precursor components may be mixed with the microspheres in the first mixing stage, and mixing stages may be performed together in a single mixing operation.

IMPROVEMENTS IN INSULATING MATERIALS

This invention relates to improvements in insulating materials, and in particular to methods for pre-use handling of thermal insulation materials for pipes and structures for example in offshore gas or oil installations.

It is often necessary to provide thermal insulation for gas or oil pipes and flow lines used in petrochemical installations, both sub-sea, and also onshore in high latitudes, to prevent excessive cooling of the product flowing through the pipelines. Such cooling tends to adversely increase the viscosity of liquid product and thus reduce the flow rate, even if condensation of any fraction (such as water hydrates or waxes) from the gas or oil stream is avoided.

Accordingly, it has become the practise to clad pipes and flow lines particularly sub-sea, for liquid or gas petroleum products, in a jacket of a synthetic plastics material which is several centimetres, typically 20-200 mm thick. This jacket is often made of a syntactic polyurethane composition, that is a polyurethane composition, which includes a substantial proportion of microspheres which may be plastics or glass spheres, these both in many cases being hollow microspheres sometimes referred to as micro-balloons, of typical diameter 75 to 150 microns.

The practise to date has been for the polyol and diisocyanate precursors of the polyurethane to be transported to the site of use in separate containers, and then mixed at the point of use, and the reacting

mixture either applied to the pipe in a moulding or casting operation, or used to cast or mould shells to be used subsequently to clad such pipes, the mixture in all cases reacting to a solid composition. The microspheres have customarily been added by the formulator to the polyol precursor. The alternative of adding the microspheres to the diisocyanate precursor whilst possible is contraindicated in many cases as the glass beads in particular provide active hydroxyl (-OH) sites which during prolonged contact will react to a significant extent with the diisocyanate, thereby reducing the functionality of the diisocyanate precursor component.

A major problem, which has been encountered with the addition of microspheres to the polyol component, results from the differences in density of the liquid polyol component and the microspheres, and the delay encountered between formulation and use due to storage and long haul transportation. Due to the lower density of the microspheres, these tend to migrate to the top of the storage container and form a thick crust on the polyol component. To enable the polyol component including the syntactic microspheres to become useable it is necessary to break up the crust and re-mix the microspheres with the liquid polyol, which is difficult and time consuming involving special on site mixing equipment, and is an unwelcome burden on the user. It is an object of the invention to provide a method for the pre-use handling of syntactic polyurethane precursor materials which effectively solves the problem of separation of the microspheres component

from the polyol component in transit or storage, and preferably allows more microspheres to be added, giving better insulation properties to the resulting composition.

According to the invention, a method of preparing a syntactic polyurethane composition for use comprises a carrying out, immediately prior to use, separate mixing steps one comprising mixing microspheres with at least one precursor of the polyurethane compound, and another mixing step comprising mixing the other precursor compound of the polyurethane with said microspheres and first precursor compound and applying the reacting mixture to the site of use.

Preferably said mixing steps are carried out concurrently, or said other mixing step immediately before after said one mixing step, and the reacting mixture is applied to the site of use as said other mixing step is proceeding or immediately after completion of the other mixing step. The mixing steps, and the step of applying the reacting mixture to the site of use are preferably carried out continuously and concurrently in a continuous or semi-continuous process.

In a first method according to the invention, the microspheres and a cross-linker may be mixed in with the polyol precursor component in the first mixing step, degassed and then the diisocyanate component added in the second mixing step, and the mixed syntactic polyurethane passed to the moulding step. In a variation of this method, the cross-linker may be added

at the second mixing step instead of during the first mixing step. In a second method according to the invention, both the polyol and the diisocyanate components are mixed separately in the first mixing step with microspheres, the mixtures are degassed, and then combined in the second mixing step to provide a reacting polyurethane mixture which is then passed to the application or moulding step. Cross-linker may again be added to the polyol component in the first mixing step, or to the complete mixture in the second mixing step.

In a third method according to the invention, the polyol and diisocyanate precursor components, and the microspheres and cross linker may all be introduced to a mixer in a single mixing stage and blended in a single mixing operation wherein the first and second mixing steps are preformed together in a single stage, the mixture degassed and passed to the moulding step. The polyol component may however be supplied pre-blended with the cross linker.

The microspheres may comprise any of the types of microspheres used for making syntactic compositions, for example, hollow plastic microspheres, or hollow glass spheres, and ceramic beadlets.

The term "polyol precursor component" refers not only to polyol materials suitable to form polyurethane's, but also amines, catalyst, pigment and other additives as used in the art to form polyurethane compositions when mixed with suitable multifunctional isocyanates.

A suitable mixer for carrying out each of the mixing stages to incorporate the dry microspheres into a liquid component is available from the Edge Sweets Company as the FFH System, and is described in US Patent No. 5332309. Another suitable mixer is supplied by Respecta-KWM GmbH.

The invention will now be further described by way of example with reference to the accompanying drawings, wherein Figures 1 to 5 are diagrams illustrating five alternative methods according to the invention.

In accordance with the alternative preferred methods of the invention, the components for the preparation of a syntactic polyurethane composition are transported in separate containers to a location close to the site of use for mixing at the location. The separate components comprise:-

1. A multifunctional isocyanate component, selected to produce a desired polyurethane composition;

2. A polyol component, comprising one or more polyol's (diol or higher which may also contain amines, catalyst, pigment and other additives), selected to produce a desired polyurethane composition on reaction with the selected isocyanate containing component;

3. A short chain low molecular weight component, reactive to isocyanate, of functionality 2 or higher, (sometimes referred to as a cross linker) which gives superior physical properties to the resultant polyurethane's, (if used)

4. Microspheres, preferably hollow glass or plastics microspheres, although other materials may as set out above be used.

As shown in figure 1, a first method according to the invention comprises feeding a polyol polyurethane precursor component via line 10 and hollow glass microspheres via line 11 to a mixer MIXER I, together with preferably a cross linker component via line 12. The polyol, microspheres and any cross linker are mixed in a mixer and fed by line 13 to a degasser 14, where as far as possible air and other entrained gasses are eliminated. It is desirable to do this, as air bubbles trapped in the foam are, at sub-sea pressures compressed thereby reducing the thickness and insulating capacity of the foam. After degassing, the mixture is passed via line 15 to a second mixer MIXER II, where the isocyanate containing component is fed in by line 16. Alternatively to being introduced at MIXER I, the cross-linker component may be also fed to MIXER II, via line 17 (broken line). The completed syntactic polyurethane mix, now beginning to react is fed via line 18 to the moulding step, to be completed within the time allowed by the reaction rate established by the polyurethane formulation.

In Fig 1, if the materials from lines 15, 16 and 17 (if used) are delivered to MIXER II in the correct proportions for forming the syntactic polyurethane composition, then MIXER II can be simply a mixing device otherwise mixer II can consist of a proportioning machine with short-term storage tanks, proportioning pumps and a suitable mixing device.

As shown in Figure 2, an alternative method according to the invention comprises not only adding microspheres introduced by line 20 to a mixer, MIXER I, with polyol component via line 21 and cross-linker component via line 22; but also adding further microspheres via line 23, to the isocyanate containing component supplied by line 24 to a further mixer MIXER II. The mixed output from MIXER I is passed by line 25 to a degasser 26, and by a line 27 to the third mixer MIXER III whilst the mixed output from MIXER II is passed via line 28 to a degasser 29 and after degassing by line 30 to the third mixer MIXER III. The output from Mixer III is then passed via line 31 to the moulding step, the polyurethane forming reaction having been initiated. An advantage of this method is that a higher total proportion of microspheres can be introduced into the formulation than by adding the microspheres only to one component. In conventional batch manufacture, due to the difficulties in the stability and separation of isocyanate/microsphere blends it is usual only to add microspheres to the polyol component. A factor limiting the proportions of microspheres, which can be added to the polyol component, is the resultant viscosity of the blend. By this method microspheres can also be added to the isocyanate stream thus the total content of microspheres in the formulation can be increased, and the effectiveness of the resultant polyurethane as thermal insulation on the pipeline improved.

In Fig 2 if the materials from lines 27 and 30 are delivered to MIXER

III in the correct proportions for forming the syntactic polyurethane composition, then MIXER III can be simply a suitable mixing device. Otherwise MIXER III can consist of a proportioning machine with short-term storage tanks, proportioning pumps, and a suitable mixing device.

Figure 3 illustrates a yet further alternative method of the invention, wherein polyol component, microspheres, cross-linker component, and diisocyanate component are all fed into a single mixer IV, via respective lines 32, 33, 34 and 35. The mixed output from mixer 31 passes to degasser 36 and hence to the moulding or casting step.

In figure 4 polyol, cross linker and diisocyanate components are fed by respective lines 41, 42, 43 to a mixer I, and the resulting mixture, which is beginning to react, is then fed via line 44 to mixer II where microspheres are added via line 45.

The mixture of microspheres with the reacting polyurethane mix is then fed by line 46 to a degasser 47, and after degassing supplied to the moulding operation by line 48.

In a further embodiment illustrated in figure 5, polyol polyurethane precursor component is fed by line 51 and cross linker by line 52 to a first mixer, mixer I, and the resulting mixture fed to a second mixer, mixer II by line 53, where it is mixed with microspheres which are added to the second mixer via line 54. The mixture is then fed by line 55 to a degasser 56, and after degassing by line 57 to a third mixer, mixer III, where the diisocyanate

polyurethane precursor component is added to the mixture of polyol, microspheres and cross linker, via line 58. The polyurethane forming condensation reaction is now initiated and the reacting mixture is fed by line 59 to the moulding stage.

The mixers used in figures 1 to 3 may be as described in US Patent No 5332309 and supplied by the Edge Sweets Company as the FFH System. The mixers used in figures 4 and 5 may be as supplied by Respecta-KWM GmbH.

In any of the above methods, the cross linker maybe pre-blended into the polyol component instead of being fed separately to the mixer. The method according to the invention allows for syntactic polyurethane's to be pre-compounded, and made up for transportation into separate polyol and diisocyanate components, and with the microspheres or other filler, and a cross-linker also to be kept separate, whilst avoiding the problem of separation, which arises when microspheres are pre-incorporated into the polyol component. A compact and transportable mixing unit, suitable for mixing the polyurethane precursor components and the microspheres as a dry filler, which can advantageously be a mixer according to the said US Patent No. 5332309 such as the Edge Sweets Company FFH System, can be made available, either to replace the wet mixer which would be needed at the mixing site in any case to blend the precursor components into a reaction mixture for the production of the polyurethane, or to feed the

polyol side of such a wet mixer, thus providing syntactic insulation applied either by moulding or casting directly onto lengths of oil or gas pipeline, or by casting or moulding insulating shells to be used subsequently to clad oil or gas pipelines. This avoids the need to reconstitute probably less insulating polyol compositions, which have separated in the time between manufacture of the polyol composition and its use in the moulding or casting operation.

Claims

1. A method of preparing a syntactic polyurethane composition for use, comprising a carrying out, immediately prior to use, a separate mixing steps one comprising mixing microspheres with at least one precursor of the polyurethane compound, and another mixing step comprising mixing the other precursor compound of the polyurethane with said microspheres and first precursor compound, and applying the reacting mixture to the site of use.

2. A method according to claim 1, wherein said one and other mixing steps are carried out concurrently, or said other mixing step immediately before or after said one mixing step and the reacting mixture is applied to the site of use as said other mixing step is proceeding or immediately after completion of said other mixing step.

3. A method according to claim 1 or 2 carried out at or close to the site of use wherein said one and other mixing step and said step of applying the reacting mixture are carried out continuously and concurrently.

4. A method according to anyone of claims 1 to 3 wherein the microspheres are mixed with the polyol precursor component in said one mixing step and the diisocyanate component added thereto in said other mixing step.

5. A method according to anyone of claims 1 to 3 wherein the polyol

and the diisocyanate component are in said one mixing step, each mixed separately with microspheres, and the resulting mixtures combined in said other mixing step.

6. A method according to anyone of claims 1 to 3 wherein said one and other mixing steps are performed together by mixing the polyol and diisocyanate polyurethane precursor components and the microspheres in a single stage.

7. A method according to any preceding claim wherein a cross-linker is added during the said one step.

8. A method according to anyone of claims 1 to 6, wherein a cross-linker is added during the other mixing step.

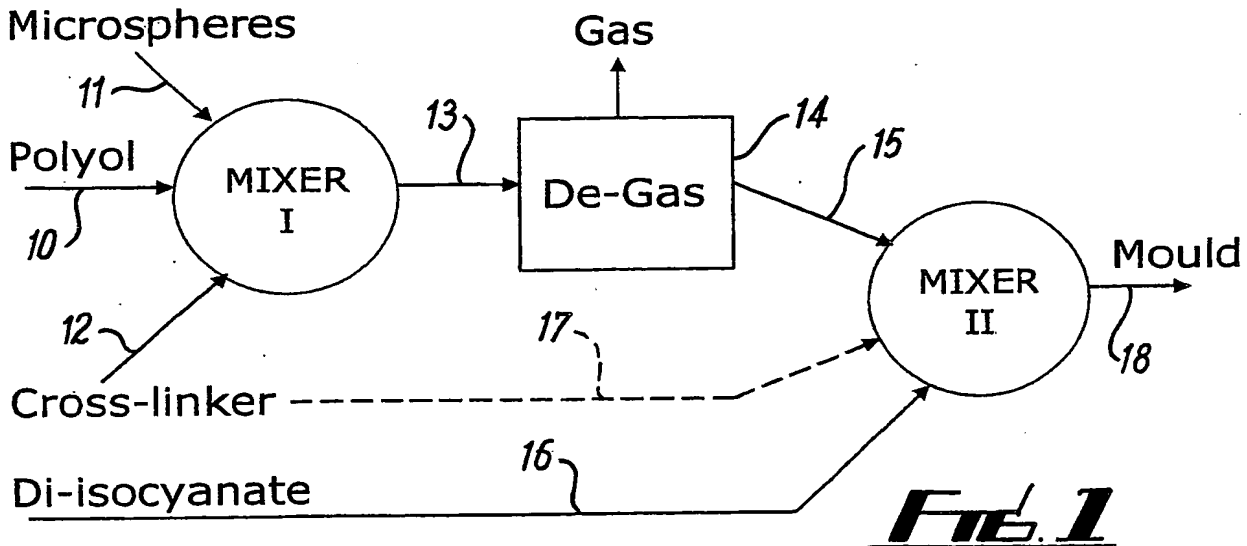
Microspheres
11
Polyol
10
MIXER I
12
Cross-linker
13
Gas
De-Gas
14
15
MIXER II
Mould
18
17
16
Di-isocyanate

FIG. 1

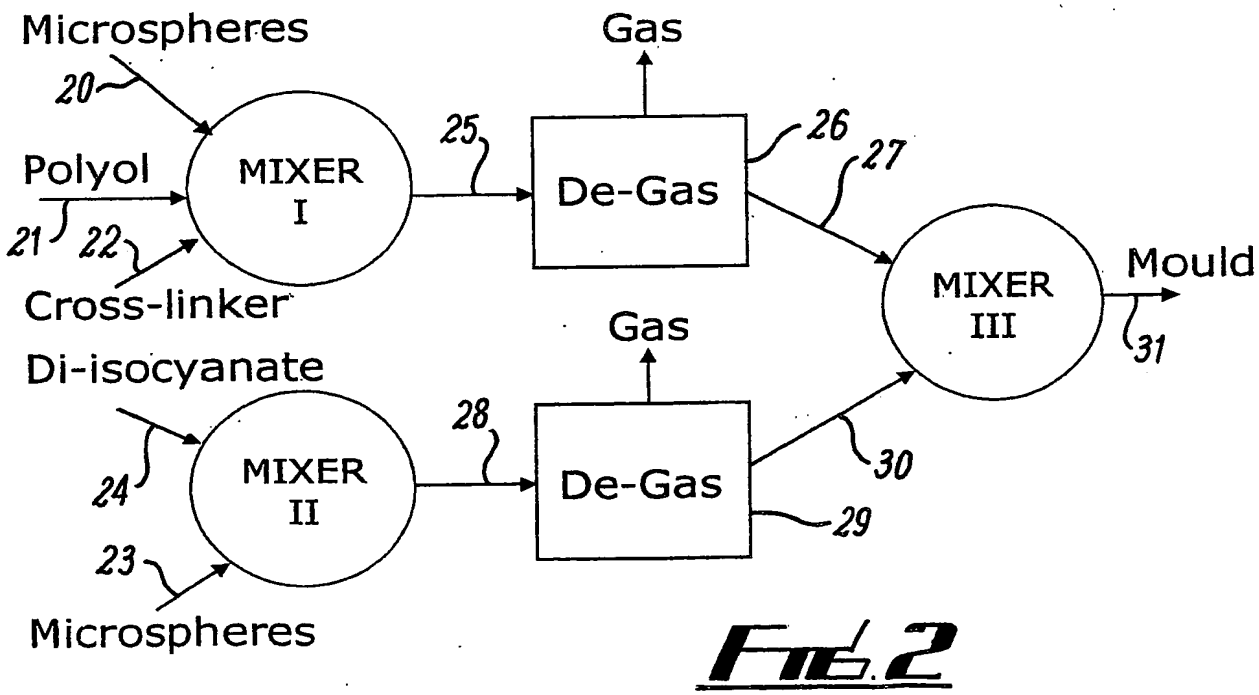
Microspheres
20
Polyol
21
22
Cross-linker
MIXER I
25
Gas
De-Gas
26
27
MIXER III
Mould
31
Gas
Di-isocyanate
24
MIXER II
23
Microspheres
28
De-Gas
30
29

FIG. 2

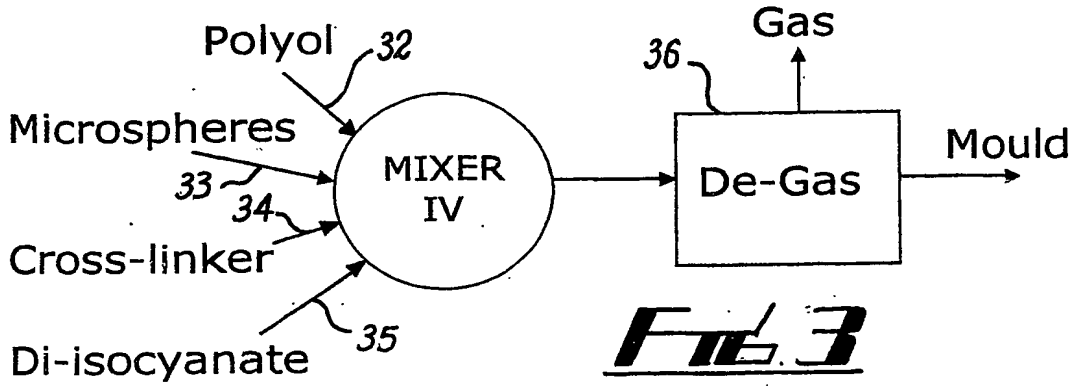

FIG. 3

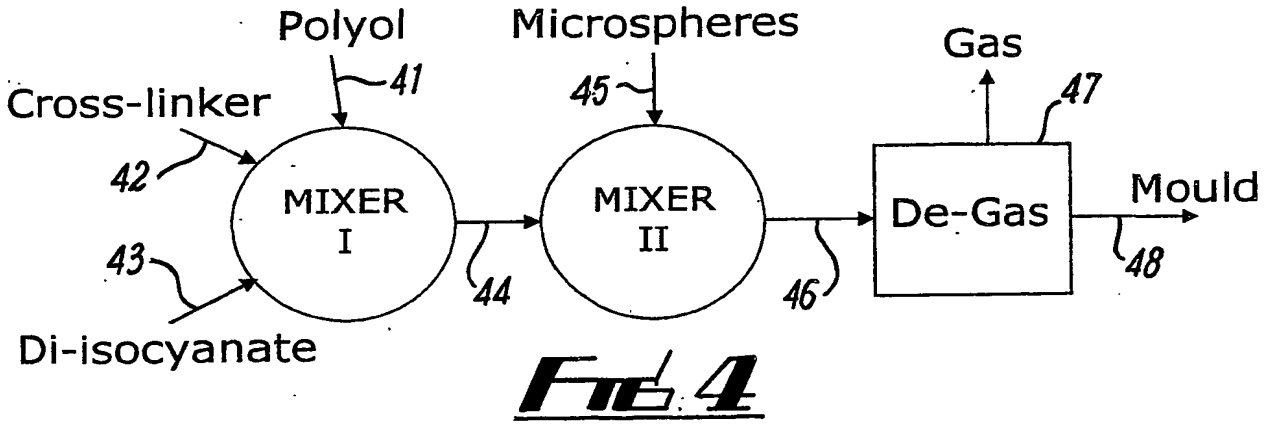

FIG. 4

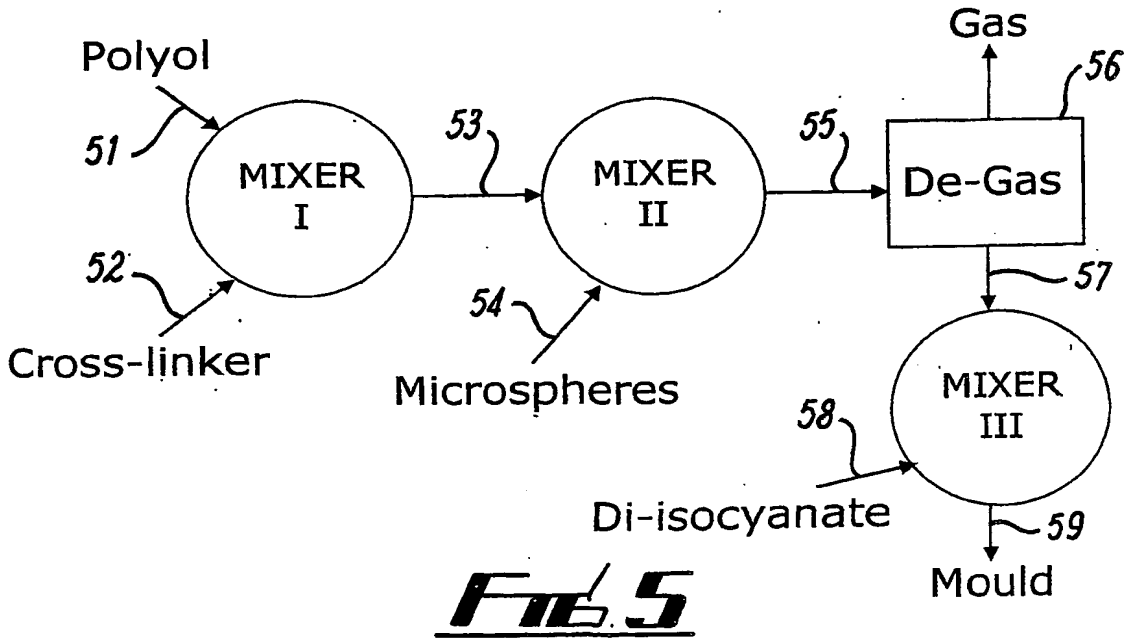

FIG. 5

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/GB 02/00946

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L75/04 C08K7/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 744 842 A (WEBSTER GEORGE A ET AL) 17 May 1988 (1988-05-17) column 1, line 31 - line 57 column 3, line 24 - line 42	1-8
X	WO 94 20286 A (ARNOTT THOMAS CHRISTOPHER) 15 September 1994 (1994-09-15) page 1, line 4 - line 11 page 5, line 33 -page 6, line 15	1-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 June 2002	26/06/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Müller, M

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 02/00946

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4744842 A	17-05-1988	AU 589940 B2	26-10-1989
		AU 5227586 A	23-07-1987
		DK 21286 A	18-07-1986
		EP 0188340 A1	23-07-1986
		JP 61223397 A	03-10-1986
		NO 860137 A	18-07-1986
WO 9420286 A	15-09-1994	AU 6149294 A	26-09-1994
		WO 9420286 A2	15-09-1994